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## DESCRIPTION

PROCESS FOR PREPARING BATTERY AND BATTERY USING SAME

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## TECHNICAL FIELD

The present invention relates to a process for preparing a battery. More particularly, the present invention relates to a process for preparing a lithium secondary battery.

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## BACKGROUND ART

Presently, lithium ion secondary batteries are being actively upgraded as a suitable secondary battery for achieving high voltage and high energy density. Major components thereof are a rolled out electrode comprising an electrode which has a pair of positive and negative electrodes, and a separator which separates each electrode for preventing short-circuit, and an electrolytic solution filled to the rolled out electrode. Practically used lithium secondary batteries are prepared according to procedures comprising laminating and winding the both of the positive, negative electrodes together with a separator to be packaged, filling an electrolytic solution and sealing the battery. Examples of these preparation processes are found in Japanese Unexamined Patent Publication No. 334884/1998 and the like.

An ideal amount of an electrolytic solution is such that voids in the porous positive, negative electrodes and separator are suitably filled with the electrolytic solution. The above procedures, however, cause the electrolytic solution to be filled into spaces irrelevant to the function of a battery, for example, into voids between the outer can and

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the electrode, and into the gap of the roll formed by lamination winding of the electrode. Since the electrolytic solution is present even in the spaces irrelevant to the battery function in this way, the electrolytic solution accounts for remarkably more than a desired amount, being the  
5 reason of weight increase.

The electrolytic solution present in the spaces irrelevant to the battery function flows and leaks more easily compared to the electrolytic solution retained in the pores of the electrodes and the separator. Therefore, it can be the reason for troubles with liquid leak  
10 of the battery.

As mentioned above, it is preferable to lessen the amount of the electrolytic solution in the spaces irrelevant to the battery function from the viewpoints of weight-wise as well as preventing the battery liquid from leaking.  
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#### DISCLOSURE OF INVENTION

The present invention has been carried out in order to solve the above problems. The object of the present invention is to provide a battery which has an extremely small amount of electrolytic  
20 solution in the above spaces irrelevant to the battery function. The present inventors have studied on processes for preparing a battery in an effort to obtain a downsized, lightweight battery with high performance, and completed the following process and device for preparing a battery as well as a battery.

25 The present invention relates to:  
a process for preparing a battery comprising,  
(i) filling an electrolytic solution to a rolled out electrode,

(ii) removing part of the electrolytic solution on the rolled out electrode to which the electrolytic solution is filled, and

(iii) packaging the rolled out electrode from which the electrolytic solution is partly removed (Claim 1);

5 the process for preparing a battery of Claim 1, wherein the rolled out electrode is immersed in the electrolytic solution to fill the electrolytic solution thereto (Claim 2);

10 the process for preparing a battery of Claim 1, wherein part of the electrolytic solution on the rolled out electrode is removed under air current (Claim 3);

the process for preparing a battery of Claim 3, wherein jetting air through a nozzle is applied to the rolled out electrode (Claim 4);

the process for preparing a battery of Claim 4, wherein the jetting air-applied positions of the rolled out electrode are changed (Claim 5);

15 the process for preparing a battery of Claim 3, wherein air current is applied to the rolled out electrode by depressurizing one side of a flow channel in which the rolled out electrode is inserted (Claim 6);

20 the process for preparing a battery of Claim 3, wherein air current is applied to the rolled out electrode by pressurizing one side of a flow channel in which the rolled out electrode is inserted (Claim 7);

the process for preparing a battery of Claim 1, wherein part of the electrolytic solution on the rolled out electrode is removed by contacting thereto an object capable of absorbing and retaining the electrolytic solution (Claim 8);

25 the process for preparing a battery of Claim 1, further comprising, diluting part of the electrolytic solution on the rolled out electrode by using a solvent which is mutually soluble with the electrolytic solution

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(Claim 9);

the process for preparing a battery of Claim 9, wherein a solvent for the electrolytic solution comprises the solvent which is mutually soluble with the electrolytic solution (Claim 10);

5 a device for preparing a battery, comprising

(i) means for filling an electrolytic solution to a rolled out electrode,

(ii) means for removing part of the electrolytic solution on the rolled out electrode to which the electrolytic solution is filled, and

10 (iii) means for packaging the rolled out electrode from which the electrolytic solution is partly removed (Claim 11); and

a battery prepared according to the process for preparing a battery of Claim 1 (Claim 12).

#### BRIEF DESCRIPTION OF DRAWINGS

15 Fig. 1 is a schematic view outlining the step for removing part of an electrolytic solution on a rolled out electrode by applying a jetting air through nozzles according to one embodiment of the present invention.

Fig. 2 is a schematic view outlining the shape of a nozzle  
20 having a slit exhaust port according to one embodiment of the present invention.

Fig. 3 is a schematic view outlining the shape of a nozzle having an exhaust port with array of holes according to one embodiment of the present invention.

25 Fig. 4 is a schematic view outlining the step for removing part of an electrolytic solution on a rolled out electrode by means of air current generated by depressurizing one side of a flow channel into

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which the rolled out electrode is disposed.

In Fig. 1 numeral 1 indicates rolled out electrode, numeral 2 indicates a nozzle which jets gas out and numeral 3 indicates jetting air.

In Fig. 2 numeral 2 indicates a nozzle which jets gas out and  
5 numeral 3 indicates jetting air.

In Fig. 3 numeral 2 indicates a nozzle which jets gas out and numeral 3 indicates jetting air.

In Fig. 4 numeral 1 indicates a rolled out electrode, numeral 3 indicates air current and numeral 4 indicates a flow channel of the air  
10 current.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The embodiments of the present invention are explained  
below.

15 The process for preparing a battery of the present invention comprises (i) filling an electrolytic solution to a rolled out electrode obtained by unifying a positive electrode, a negative electrode and a separator, (ii) removing part of the electrolytic solution on the rolled out electrode to which the electrolytic solution is filled and (iii) packaging  
20 the rolled out electrode from which the electrolytic solution is partly removed. The steps are explained in detail below.

The rolled out electrode of the battery is obtained by unifying a positive electrode, a negative electrode and a separator including, for example, those prepared by lamination and winding of a positive  
25 electrode sheet, a negative electrode sheet and a separator film for separation thereof. Adhesion of laminated, wound elements by a resin or the like, or fixation on the exterior with tape or the like brings about a

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rolled out electrode as an independent structure.

Useful as the positive electrode is, for example, the one obtained by applying powdery lithium cobaltate onto a piece of aluminum foil using poly(vinylidene fluoride) as a binder and by drying. Useful as the negative electrode is, for example, the one obtained by applying powdery graphite carbon onto a piece of copper foil using poly(vinylidene fluoride) as a binder and by drying. A porous polyethylene film can be used as the separator.

A battery comes to function when the rolled out electrode, the independent structure, is charged with an electrolytic solution. As the electrolytic solution, for example, the one obtained by dissolving an electrolyte into any solvent can be used. The useful solvent for the electrolytic solution includes, for example, a mixed solvent of ethylene carbonate and dimethyl carbonate. Examples of the electrolyte are lithium hexafluorophosphate and the like.

Filling of the electrolytic solution can be performed outside the outer package of the battery. It is difficult to immerse and fill the electrolytic solution efficiently to the innermost of the rolled out electrode when the rolled out electrode is relatively large or when a dense layer exists in the electrode. The electrolytic solution can be efficiently immersed and filled thereto at a high filling rate by depressurizing or centrifuging the rolled out electrode in a state of complete sinking beneath the electrolytic solution. The depressurization pressure can be, for example, a little higher than the pressure which causes depressurization boiling of the electrolytic solution. Centrifugal force can be, for example, such that rotational speed of 4 G, about four times the gravity, is thereby generated.

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When the rolled out electrode filled with the electrolytic solution is taken out from the electrolytic solution, it holds some electrolytic solution irrelevant to the battery function (extra electrolytic solution) on the outside or in a gap of the roll. It is preferable to decrease the extra electrolytic solution as much as possible since it causes weight increase and liquid leak.

Partial removal of the electrolytic solution on the rolled out electrode to which the electrolytic solution is filled enables to decrease the amount of the extra electrolytic solution present in the spaces irrelevant to the battery function. Part of the electrolytic solution on the rolled out electrode can be removed by applying air current to the rolled out electrode. In case of the partial removal of the electrolytic solution on the rolled out electrode under air current, dry air or dry nitrogen, for example, is available as a gas which generates the air current. The dry air and the dry nitrogen do not harm the battery performances.

Processes for removing the extra electrolytic solution includes a process for spraying fast air current. The application of jetting air through the nozzle to the rolled out electrode enables to remove part of the electrolytic solution on the rolled out electrode. An outline of the step for removing part of an electrolytic solution on a rolled out electrode by applying the jetting air through nozzles is shown in Fig. 1. The spraying of the jetting air through the nozzles to the surface of the rolled out electrode results in removal of the electrolytic solution thereon by the pressure.

It is possible to remove the extra electrolytic solution efficiently all over the rolled out electrode by changing (scanning) the

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position at which removal strength of the electrolytic solution is high, namely, the position received the direct air current in application of the jetting air through the nozzle to the rolled out electrode. Scanning for the positions received the direct air current can be performed by moving the rolled out electrode or the nozzle in application of the jetting air through the nozzle to the rolled out electrode. The scanning rate can be, for example, about 5 cm per second.

Preferably, the jetting air through the nozzle ranges in angle from 30 to 90° to the normal line of the electrolytic solution-removed plane of the rolled out electrode. When it is less than 30°, the droplets do not disperse in one direction causing to increase the possibility of polluting the surface from which the electrolytic solution has already been removed.

Preferable as a nozzle are those having a slit exhaust port which jets air out or an exhaust port which jets air out through array of holes for sending out band-shaped air current. An outline of the nozzle having a slit exhaust port is shown in Fig. 2. An outline of the nozzle having an exhaust port with array of holes is shown in Fig. 3.

The jetting out rate of the air current through the nozzle can be, for example, about 40 m per second. When the jetting out rate of the air current through the nozzle is too slow sufficient removal of the extra electrolytic solution tends to be difficult. When it is too fast the rolled out electrode may be deformed by means of the air current pressure.

Processes for removing the extra electrolytic solution includes a process for applying fast air current through a flow

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channel to the rolled out electrode being disposed inside the flow channel. The flow rate of the air current through the flow channel can be, for example, 20 m per second. When the flow is too fast, the rolled out electrode tends to be deformed. When it is too slow, sufficient removal of the extra electrolytic solution tends to be difficult.

The air current can be formed by sending gas from one side of the flow channel or by depressurizing one side of the flow channel with the rolled out electrode being disposed therein. An outline of the step for removing part of an electrolytic solution on a rolled out electrode by means of air current generated by depressurizing one side of a flow channel is shown in Fig. 4.

Processes for removing the extra electrolytic solution includes a process for contacting an object capable of absorbing the electrolytic solution. Useful as the object capable of absorbing and retaining the electrolytic solution are, for example, a liquid-absorbent non-woven fabric, woven fabric, sponge resin and the like.

Packaging the rolled out electrode from which part of the applied electrolytic solution is removed enables to prepare a battery, wherein the extra electrolytic solution irrelevant to the battery function is remarkably reduced. Useful as the outer can is, for example, a metal can made of stainless or aluminum or an aluminum laminated film.

According to the present invention, lightweight of batteries can be achieved and possibility of liquid leak can be remarkably decreased by reducing the extra electrolytic solution.

In some case, solid content in an electrolytic solution may remarkably precipitate onto the surface of a rolled out electrode in

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accordance with vaporization of a solvent through the removal process of the extra electrolytic solution, depending on kinds of electrolytic solution. Preparation of batteries by using the rolled out electrode on which the solid content is precipitated may cause  
5 unevenness of the outer can surface, and may result in unfavorable appearance.

Precipitation of the solid content can be reduced by diluting part of the electrolytic solution on the rolled out electrode by using a solvent (cleaning solvent) which has less solid content than the  
10 electrolytic solution and is mutually soluble with components of the electrolytic solution. For example, part of the electrolytic solution on the rolled out electrode can be diluted by washing the rolled out electrode with the cleaning solvent.

Available as the cleaning solvent are solvents in which no or  
15 little solid content is dissolved including a solvent having less solid content than the electrolytic solution, while it is also possible to use a solvent which does not affect the battery performances or which is mutually soluble with the electrolytic solution. For example, a solvent obtained by removing a solute such as salt from the components of the  
20 electrolytic solution can be preferably used since it does not affect battery performances. Examples of the useful cleaning solvent are diethyl carbonate, dimethyl carbonate, methyl ethyl carbonate, propylene carbonate, caprolactone and the like.

Washing of the rolled out electrode with these kinds of  
25 solvent before or after the removal step of the extra electrolytic solution can prevent the solid content from precipitating.

According to the process for preparing batteries of the

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present invention, the electrolytic solution irrelevant to the battery performances is decreased, making it possible to prepare a battery which is light, hard to leak liquid and has no problems with battery performances or appearance.

5           The device for preparing batteries according to the present invention comprises (i) means for filling an electrolytic solution to a rolled out electrode obtained by unifying a positive electrode, a negative electrode and a separator, (ii) means for removing part of the electrolytic solution on the rolled out electrode to which the electrolytic solution is  
10   filled, and  
(iii) means for packaging the rolled out electrode from which the electrolytic solution is partly removed.

          The means for filling an electrolytic solution to a rolled out electrode has, for example, a tank for electrolytic solution used for  
15   immersion of the rolled out electrode in the electrolytic solution. The means for removing part of the electrolytic solution on the rolled out electrode has, for example, nozzles jetting gas out , a flow channel and a fan or depressurization device for forming air current, or a substance capable of absorbing the electrolytic solution.

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## EXAMPLES

While the present invention is explained in detail through examples below, the present invention is not limited thereto.

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### EXAMPLE 1

(Preparation of electrolytic solution)

Powdery  $\text{LiPF}_6$  as a support salt was dissolved into a solvent

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obtained by mixing ethylene carbonate and dimethyl carbonate in a weight ratio of 1:1 to adjust it to 1 mol/l.

(Preparation of electrodes)

Positive electrode material was prepared by applying a paste  
5 of a positive electrode active material obtained by mixing 87 % by weight  
of an active material,  $\text{LiCoO}_2$ , 8 % by weight of a conductive graphite  
powder, 5 % by weight of poly(vinylidene fluoride) as a binder resin and a  
solvent, N-methylpyrrolidone (hereinafter referred to as "NMP") onto a  
current terminal comprising a piece of 20- $\mu\text{m}$ -thick aluminum foil  
10 according to Doctor Blade method in a thickness of about 200  $\mu\text{m}$ ,  
drying the same, and further, by rolling it to 120  $\mu\text{m}$  thick.

A negative electrode material was prepared by applying and  
drying a paste of a negative electrode active material obtained by mixing  
95 % by weight of mesophase microbeads carbon (available from Osaka  
15 Gas Co., Ltd.), 5 % by weight of poly(vinylidene fluoride) as a binder resin  
and a solvent, NMP onto a current terminal comprising a piece of 12-  
 $\mu\text{m}$ -thick copper foil according to Doctor Blade method in a thickness of  
about 200  $\mu\text{m}$ , and further, rolling it to 120  $\mu\text{m}$  thick.

The thus prepared positive and negative electrode materials  
20 were cut into a size of 50 mm  $\times$  200 mm and current collector terminals  
were attached to the ends.

(Formation of rolled out electrode)

A separator cut into a size of 52 mm  $\times$  210 mm (available from  
Höchst Celanese Co., Ltd.; Trade-name: CELLGUARD#2400) was  
25 interposed between the positive electrode and the negative electrode. It  
was rolled out with the lamination maintained, flattened and fixed with a  
strip of adhesive tape to obtain a plane, wound construction. The

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number of the rolling was adjusted so that the width is about 50 mm when flattened.

(Injection of electrolytic solution)

A rolled out electrode was disposed in an electrolytic solution.

- 5 The whole was depressurized with a pump and maintained at 50 torr for 3 minutes, and then the atmospheric pressure was recovered.

(Removal of extra electrolytic solution)

- 10 The electrolytic solution was removed by applying dry jetting air through 70-mm-long and 0.3-mm-wide slit nozzles in one liter per second in terms of the atmospheric pressure. The jetting air was applied at a slope of 45° to the normal line of the rolled out electrode surface while distance from the nozzle tip to the rolled out electrode surface was set to 5 mm. Removal was performed by scanning the rolled out electrode from one end to the other end at a speed of 5 cm per  
15 second. The both surfaces of the rolled out electrode underwent the above procedure.

A very small amount of solid precipitation was observed on the rolled out electrode surface after the removal procedure of the extra electrolytic solution.

- 20 (Outer packaging using aluminum laminated film)

The rolled out electrode prepared through the above procedure was kept under reduced pressure of about 50 torr and an aluminum laminated film was used for sealing to form an outer package.

- 25 A piece of 50- $\mu$ m-thick aluminum foil, 12- $\mu$ m-thick polyethylene terephtharate film and 5- $\mu$ m-thick polyethylene film were laminated, and it was cut into a size of 70 mm  $\times$  120 mm to be used as an aluminum laminated film. The film was folded in half, 70 mm  $\times$  60 mm,

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and three remaining edges were closed by heat-sealing with the rolled out electrode therein.

(Evaluation of liquid leak)

5 A hole having a diameter of 2 mm was made at the edge of the outer package and the package was kept with the hole downward for 5 minutes to estimate the amount of the leaked electrolytic solution according to the weight change before-and-after the keeping.

10 The battery prepared through the above process was 13.5 g in weight and showed 0.05 g of liquid leak according to the liquid leak evaluation.

## EXAMPLE 2

(Case of disposition in flow channel)

15 There was provided a cylindrical flow channel in which 0.5 mm of space is formed between the flow channel inner wall and the rolled out electrode when the battery rolled out electrode was placed inside. The rolled out electrode was fixed on the inside of the flow channel to remove the extra electrolytic solution by applying dry air current to the space between the flow channel and the rolled out electrode. The amount of the dry air was adjusted so that the pressure difference was 0.5 kgf/cm<sup>2</sup> between the upper side and the lower side.

20 A battery was prepared in the same manner as in Example 1 except that the extra electrolytic solution was removed according to the above process. The battery was 13.3 g in weight and showed 0.01 g of liquid leak according to the liquid leak evaluation.

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### EXAMPLE 3

(Case of using non-woven fabric)

5 A battery was prepared in the same manner as in Example 1 except that the extra electrolytic solution was removed by using a polypropylene non-woven fabric to wipe out the electrolytic solution on the outside of the post-injection rolled out electrode. The battery was 13.6 g in weight and showed 0.07 g of liquid leak according to the liquid leak evaluation. Though this process does not require any device for supplying a large amount of dry gas, it was impossible to remove the  
10 extra solution in the gap of the roll.

### EXAMPLE 4

(Case of washing by solvent)

15 A battery was prepared in the same manner as in Example 1 except that removal of the extra electrolytic solution was performed after the rolled out electrode posterior to filling of the electrolytic solution was immediately immersed in diethyl carbonate for 10 seconds.

The battery was 13.5 g in weight and showed 0.05 g of liquid leak according to the liquid leak evaluation. Such a small solid  
20 precipitation on the rolled out electrode surface as seen in Example 1 was not observed. No unevenness according to solid precipitation surfaced even after the packaging.

### COMPARATIVE EXAMPLE 1

25 An aluminum laminated film was sealed remaining one edge unsealed and it was made into a bag with the rolled out electrode interposed therebetween. An electrolytic solution was injected into the

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bag made of the package film to perform immersion of the electrolytic solution under reduced pressure. The extra electrolytic solution after the immersion was removed by pipette and then, the remaining edge was sealed to close. A battery was prepared in the same manner as in  
5 Example 1 except for the above procedures. The battery was 14.1 g in weight and showed 0.9 g of liquid leak according to the liquid leak evaluation.

As shown in this Comparative Example, removal of the extra electrolytic solution after packaging makes it difficult to reduce the extra  
10 electrolytic solution not contributory to the battery performance sufficiently. Consequently, the battery will weigh heavier while the electrolytic solution causing liquid leak will be increased.

#### COMPARATIVE EXAMPLE 2

15 An aluminum laminated film was sealed remaining one edge unsealed, and it was made into a bag with the rolled out electrode interposed therebetween. An electrolytic solution was injected into the bag made of the package film and the total weight of the battery was adjusted to 13.5 g. The weight is the same as that in Example 1. After  
20 that it was kept under 50 torr for 3 minutes followed by sealing of one remaining edge to close the battery. A battery was prepared in the same manner as in Example 1 except for the above procedures.

The battery was 13.5 g in weight as mentioned above showing 0.07 g of liquid leak according to the liquid leak evaluation. When  
25 charge-discharge tests were carried out by using this battery and the battery of Example 1 at the rate of 0.5 C, this battery accounted for about 80 % the discharge capacitance compared with the battery

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prepared in Example 1.

This is resulted from the fact that the electrolytic solution did not sufficiently fill the spaces where the electrolytic solution is needed in terms of battery performances, being present even in spaces not  
5 contributory to the battery performances.

#### EXAMPLE 5

(Case of slow air current)

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A battery was prepared in the same manner as in Example 1  
10 except that the air current was applied at a rate of 0.2 liter per second when the extra electrolytic solution was removed. Even after the removal of the extra electrolytic solution, remainder of electrolytic solution was remarkably found on the surface of the rolled out electrode. The battery was 13.9 g in weight showing 0.5 g of liquid leak according to  
15 the liquid leak evaluation. Although there were weight increase due to the extra electrolytic solution and increase of electrolytic solution leading to liquid leak compared with Example 1, remarkable effect was seen in comparison with Comparative Example 1.

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#### COMPARATIVE EXAMPLE 4

(Case of fast air current)

A battery was prepared in the same manner as in Example 1 except that the air current was applied at a rate of 2 liter per second when the extra electrolytic solution was removed.

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Peeling was partly observed among components of the rolled out electrode after the removal of the extra electrolytic solution. The battery was 13.4 g in weight showing 0.02 g of liquid leak according to

the liquid leak evaluation.

According to the preparation process of Claims 1 to 8, it is possible to prepare a light battery with less possibility of liquid leak since the amount of the extra electrolytic solution not contributory to the battery performance is small.

According to the preparation process of Claims 9 to 10, it is possible to prepare a battery having little, visually unfavorable unevenness which is caused by precipitation on the surface of the rolled out electrode.

According to the preparation device of Claim 11, it is possible to prepare a light battery with less possibility of liquid leak.

The battery according to Claim 12 has high weight energy density because the weight of the electrolytic solution is reduced and it has small possibility of liquid leak accident because the extra electrolytic solution is decreased.

#### INDUSTRIAL APPLICABILITY

The process for preparing a battery, the device for preparing a battery and the battery of the present invention can be widely applied to a battery including lithium ion battery which comprises a rolled out electrode immersed in an electrolytic solution and an outer can packaging the same.

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